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Removal of rhodamine dye from aqueous solution using Gulmohar tree fruit activated carbon

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ABSTRACT

Rhodamine B (Basic Dye) was selected as the test dye for the evaluation of the adsorption capacity of activated carbon prepared from the fruits of Gulmohar tree. Batch-mode adsorption studies were carried out by varying different parameters such as agitation time, initial dye concentration, carbon dose, particle size and pH. Desorption studies mainly carried out to elucidate the mechanism of adsorption. The time required to attain equilibrium was found to be within 75 min for all the concentrations studied (10 to 40 mg/L). The adsorption followed both Langmuir and Freundlich isotherms. The adsorption capacity was found to be 31.847 mg/g of Gulmohar tree Fruit Carbon (GTFC)at an initial pH of 5+0.2 at room temperature (30 ±2°C) for the particle size of 125-250 µm. The complete removal of the dye from 20 and 30mg/L aqueous solution was possible with 6 and 10g of the activated carbon respectively. The percent removal was increased with decrease in the particle size of the adsorbent. The influence of pH on dye removal was insignificant and a portion of the dye from the carbon was recovered in basic medium.

Key word's : Activated carbon, Gulmohar tree fruit, Adsorption capacity, Kinetics.

Introduction

The survival of mankind on earth is threatened by many problematic environmental issues. Among them, industrial effluents are of much concern because of its toxic nature to the environment. Synthetic dyes are extensively used for textile dyeing, printing in industries and colour photography. The amount of wastewater generated by textile industries alone works out to be 4,500 million kilo liters annually (Lal, 1998). The nearby water bodies are affected by discharging the textile industrial effluents (Dutta, 1994). The colour affects the nature of the receiving water bodies and inhibits the penetration of sunlight into the stream thereby reducing the photosynthetic activity(Nawar and Doma, 1989). Dyes are reported to cause some variation in the wastewater characteristics like pH, BOD and COD (Peter Cooper, 1995). Some dyes are found to be carcinogenic in nature. Hence, it is essential to remove dyes before it mixes with water bodies. Current methods for wastewater treatment include coagulation (Boon *et al.* 2000), photo catalytic-degradation (Tanaka, 2000), bio decolonization method (Kapdan *et al.* 2000). The adsorption process with activated carbon is attracted by many scientists because of the effectiveness for the removal of dyes in trace quantities. But the process has not been used extensively for its high cost. It results in a search of low cost adsorbent from agricultural and industrial waste. Such types of non-conventional adsorbents are used to include silk cotton hull (Sameena, 2003), eucalyptus bark (Morais, *et al.* 2000), orange peel(Sivaraj *et al.* 2001), and coir pith(Namasivayam *el al.* 2001).

Gulmohar tree (*Delonix regia*) is a deciduous tree. It is an avenue and ornamental plant. The flat Pod (fruit) which fits for nothing is used for the preparation of activated carbon.The objective of the present study is to investigate the adsorption capacity of the GTFC to remove Rhodamine B (Basic dye) from aqueous solution. A basic dye is selected as the test dye because it is the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high (McKay, 1982).

Materials and Methods

Adsorbent

The dried Gulmohar tree fruits collected from the campus of PSG College of Arts and Science, Coimbatore, Tamil Nadu, India were used for the preparation of activated carbon. The materials collected was cut into small pieces, dried in sunlight until the moisture was partially evaporated and was further dried in a hot air oven at 60°C for 24 h. The completely dried pods were allowed for chemical activation by the addition of concentrated sulphuric acid (1:1 w/v) with constant stirring. The charred material was kept in hot air oven at 110±5°C for I2h. The resulting material was washed with distilled water, soaked in 2% sodium bi-carbonate solution and allowed overnight to remove the residual acid from the pores of the carbon. Then the material was washed with distilled water, until the pH of the adsorbent reached a pH of 7+0.2. dried in a hot air oven at 110±5°C for 6h. The dried material was ground and the particles retained between 125 to 250 µm, 250 to 500µm and below 125µm were collected separately and used for the study. Characteristics of GTFC are presented in Table-1. All the chemicals used were of analytical reagent grade.

Adsorbate

A stock solution of 1000 mg/L dye was prepared by dissolving 1gm of Rhodaminc B dye in 1000 mL of double distilled water.

Batch mode adsorption studies

The adsorption experiments were carried out by agitating l00 mg of the adsorbent and 50 mL of dye solution of desired concentration (10-40 mg/L) at an initial pH of 5 ±0.2 and agitated in a mechanical shaker (160 rpm) for predetermined time intervals at room temperature(30± 0.2 C). The dye solution was separated out from the adsorbent by centrifugation and the absorbance was measured for the supernatant using Spectrophotometer at 565 nm. The effect of adsorbent dosage on percent removal was studied with 20 to 600 mg/50 mL of the adsorbent while maintaining the dye concentration at 20 and 30 mg/L. The effect of particle size of the adsorbent (<I25 µm, 125-250µm, 250-500µm) on the removal of Rhodamine B was carried for 20 mg/L dye concentration Langmuir isotherm was studied with different initial concentration of dye from 10 to 40 mg/L, while maintaing the adsorbent dosage at 100mg/50mL . Freundlich isotherm was obtained from the effect of carbon dosage on dye removal. Effect of pH on dye removal was studied using l00mg of carbon dose for 10 mg/L dye solution. Experiments were carried out in duplicate and the mean values were taken for calculation.

Batch mode desorption studies

Fifty milliliters of 20 mg/L of the dye was agitated with l00mg of carbon for predetermined equilibrium time (45 min). After centrifugation,the supernatant was analysed for their residual dye concentration, discarded and the adsorbent was gently washed with distilled water to remove any unadsorbed dyes. The dye laden carbons were agitated with 50 mL of hydrochloric acid (0.01 to 0.2N) and sodium hydroxide (0.01 to 0.2N) separately for 45 min.

Results and Discussion

Effect of agitation time and Initial dye concentration on adsorption

The effect of agitation time on the removal of Rhodamine B by GTFC is shown in Fig.1. The removal increases with time and attains equilibrium time within 75 min for all the concentrations studied (10 to 40 mg/L) and the curves obtained were single, smooth and continuous till the saturation of the dye onto activated carbon surface. The colour removal was decreased from 69.52 to 57.0 percent for the increase in dye concentration from 10 to 4-0mg/L in the initial stages of agitation, indicating that the dye removal by adsorption on GTFC is depend on concentration .

Adsorption kinetics

The kinetics of dye adsorption of Rhodamine B on GTFC can be studied by using a simple pseudo first order kinetic equation of the form (Stephen Inbaraj *et al.* 2002)

$$\log (qe-q) = \log q_e - \frac{k_{ad}}{2.303} t$$

Where q_e is the amount of solute adsorbed per unit weight of the adsorbent (mg/g) ai equilibrium time, q is the amount adsorbed (mg/g) at time t (min) and K_{ati} is the rate constant (L/min).Linear plots of log (q_c-q) Vs t (Fig.2) show the applicability of the above equation for the adsorption of Rhodamine B onto GTFC. The K_ad values for different initial dye concentrations (10 to 40 mg/L) were calculated from the slope of the linear plots and are presented in Table. 2

In the case of microporous adsorbents, the uptake of solute consists of the following four basic steps.

(i) Bulk transport of the solute to the hydrodynamic boundary layer surrounding the carbon particle.
(ii) Diffusive film transport through the boundary layer referred to as external or film diffusion.
(iii) Diffusive transport through the internal pores of the carbon and /or along the pore-wall surface (termed surface or intra particle diffusion)
(iv) Adsorption or attachment of the solute particle at a suitable "site" on the carbon surface.

One or more of the above steps may be the rate controlling factor. In order to find out the possibility of the dye being transported within the pores of GTFC, the amount of dye sorbed at time t, that is q was plotted against the square root of t, $t^{1/2}$, according to the equation, $q=k_p t^{1/2}$ proposed by (Weber and Morris 1962). Figure 3 shows such plots for Rhodamine B dye adsorption onto GTFC. The initial portion of dye uptake due to film diffusion could not be followed experimentally due to the fastness of dye sorption.

The second linear portion is the gradual adsorption stage attributed to intra particle diffusion effect(McKay *el al.* 1980). The third portion is final equilibrium stage. From the second linear portion (Intra particle diffusion stage), it can be concluded that intra particle diffusion process participate to a considerable amount in controlling the over all rate, as the extrapolation of the second linear portion cuts the y axis close to origin (Stephen *et al.* 2002).

The intra particle diffusion rate constant K_p (Table2) was obtained from the slope of the straight line. The K_p values increased with increase in dye concentration, which shows that the adsorption rate is governed by the diffusion of dye with in the pores of the adsorbent.

Effect of carbon dosage on Rhodamine B dye adsorption

Figure4 shows the effect of carbon dosage on Rhodamine B dye adsorption onto GTFC. The removal of dye increases with increase in carbon dosage. It was observed from the result that 20 and 30 mg/L of the dye required 6.0 and 10.0 g of the activated carbon respectively.The increase in adsorption of the dye with increase in carbon dosage was due to the exposure of more binding sites for adsorption.

Adsorption Isotherms

Langmuir isotherm can be applied for the adsorption of Rhodamine B onto GTFC(Langmuir, 1918).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{Ce}{Q_0} \qquad (2)$$

Where, C_e is the equilibrium concentration (mg/L). q_e is the amount of the dye adsorbed (mg/g), Qo and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e Vs C_c shows that the adsorption follows Langmuir isotherm models (Fig.5). The value of Q_0 and b were calculated from the slope and intercept of the plot, respectively. The values obtained were Q_0= 31.847 mg/g and b=0.0169 L/min.

The essential characteristic of Langmuir isotherm can be expressed in terms of dimensionless separation factor of equilibrium parameters R_L. It can be defined by.

$$RL = \frac{1}{1 + bC_0}$$

Where, Co is the initial dye concentration (mg/L) and b is the Langmuir constant (L/mg). The R, values indicate the type of isotherm as follows,

RL Value	Type of Isotherm
RL>1	Unfavorable
RL=1	Linear
0<RL<1	Favorable
RL= 0	Irreversible

The Freundlich equation is widely used in the environmental engineering practice to model adsorption of pollutants from an aqueous medium (Slejko, 1985). The expression for Freundlich equation is given as,

$$q_e = K_r Ce^{1/n} \qquad \text{---------} \quad (4)$$

The linear form of Freundlich equation is given by the following expression.

$$\log_{10}(x/m) = \log 10K_f + 1/n \log_{10} Ce \text{ ------- (5)}$$

Where, x is the amount of the dye adsorbed at equilibrium (ing), m is the weight of adsorbent used (mg), C_c is the equilibrium concentration of the dye in solution (mg/L).k and n are the constants incorporating all factors affecting the adsorption process. Linear plot of log x/m Vs log C_c show that the adsorption follows Freundlich isotherm (Fig.6). The Freundlich constants were K_t - 3.6694 and n= 2.1997 for 20 mg/L of the dye. The mathematical calculations of n values between 1 to 10 represent the best adsorption (Treybal, 1980).

Effect of particle size of the adsorbent on dye removal

Fig.7 shows that the percent removal of Rhodamine B dye decreased with increase in particle size of the adsorbent ranging <125 (μm 125-250 jam, 250-500 μm are 94.28, 88.57 and 81.42% respectively at equilibrium. Higher percent removal with lower particle size is due to availability of more surface area for adsorption.

Effect of pH on dye removal

Fig.8 represents the effect of initial pH from 3.0 to 9.0

Table 1. Characteristics of activated Gulmohar tree fruit carbon

Parameter	Value
pH of 1% solution	8.4
Moisture content (%)	1.371
Water soluble matter (%)	2.129
Acid soluble matter (%)	5.231
Decolourising power (mg/g)	61.5
Surface area (m^2/g)	326.57
Sodium (mg/g)	3
Potassium (mg/g)	3
Calcium as $CaCO_3$ (mg/g)	65

Table 2. Rate constants for Rhodamine B dye adsorption

Dye conc. (mg/L)	qe (mg/g)	Adsorption rate constant K_{ad} (1/min) x 10^{-2}	Intra particle diffusion rate constant x 10^{-2} (mg/g/$min^{1/2}$)
10	4.5235	5.112	16.21
20	8.857	3.689	37.70
30	12.906	5.365	55.90
40	16.8	5.711	68.65

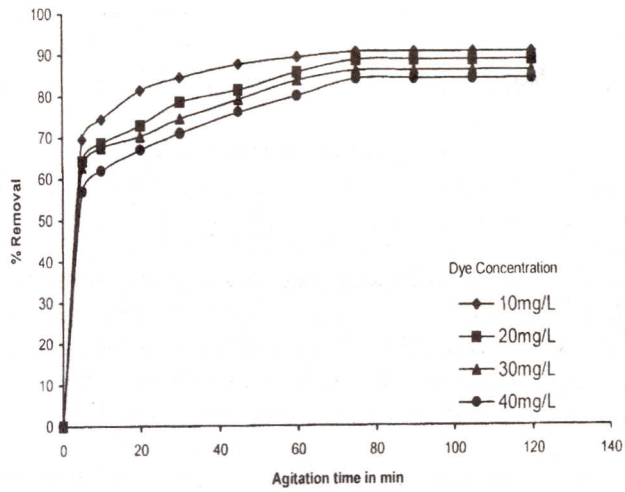

Fig. 1 Effect of agitation time and initial dye concentration on Rhodamine B adsorption

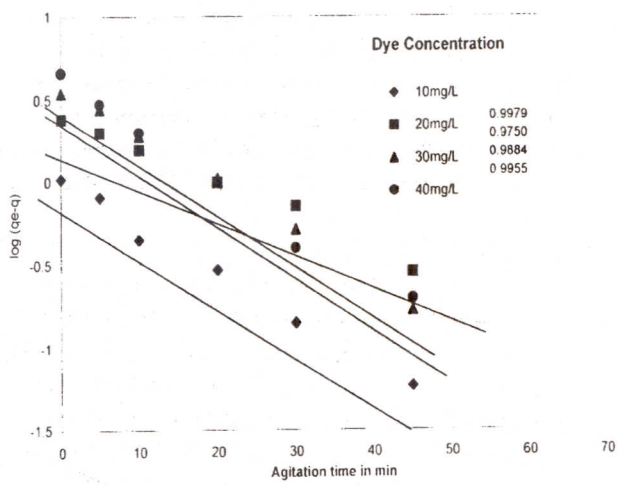

Fig. 2 Lagergren first order kinetics plots

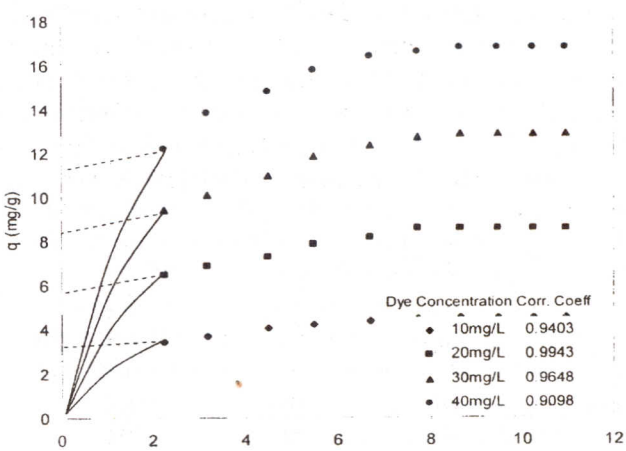

Fig. 3 Intra particle diffusion plots

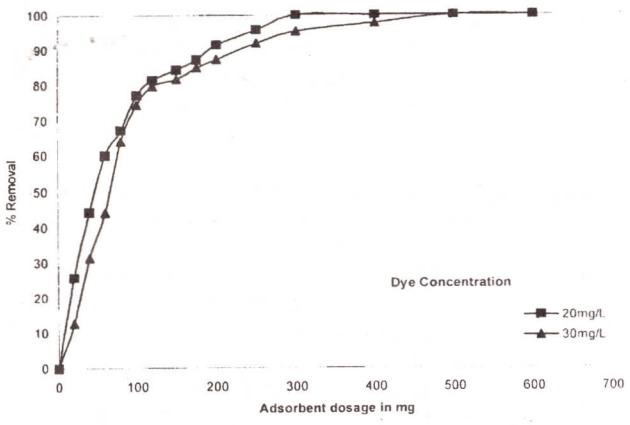

Fig. 4 Effect of adsorbent on Rhodamine B adsorption.

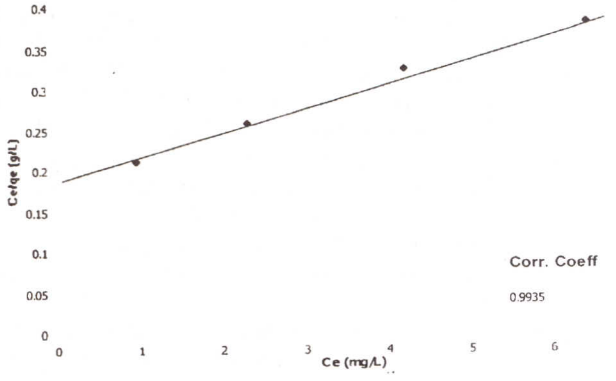

Fig. 5 Langmuir isotherm model

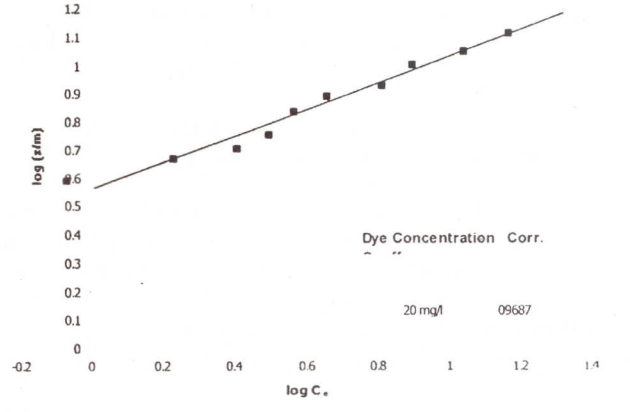

Fig. 6 Freundlich isotherm model

on the removal of dye. The study shown that there was significant change in the percent removal of dye over the entire pH range. This trend may be due to the surface of activated carbon becomes positively charged at lower Ph and this facilitates sorption of cationic dye molecules, probably by exchange sorption (Venkata Mohan and Karthikeyan, 1997). When pH values increase, the surface of activated carbon becomes negatively charged resulting in electrostatic attraction between opposite charges, which account for the observed higher level of adsorption.

Desorption studies

,Desorption studies help to elucidate the nature of adsorption and recycling of the adsorbent and the dye. The regeneration of the adsorbent may also make the treatment process economical. Attempts were made to regenerate colour from the dye laden carbon using various strengths of hydrochloric acid (0.01 to 0.2 N) and sodium hydroxide (0.01 to 0.2N) separately.There was no significant desorption of the dye from the carbon with hydrochloric acid. But with sodium hydroxide solution, there was increase in desorption from 30.76 to 53.84 percent by increasing the strength from 0.01 to 0.2 (Fig 9). This may be due to the exchange of positively charged sodium ion with the cationic dye resulting in desorption of Rhodamine B to the aqueous solution. The study further reveals that the major made of adsorption process follows is ion-exchange mechanism.

Conclusion

The activated carbon prepared from waste agricultural product, Gulmohar tree fruits was found to be effective in removing Rhodamine B dye from aqueous solution. The adsorption equilibrium time was reached within 75 min for all the concentrations studied. The adsorption followed pseudo first order kinetic equation. The data confirmed with Freundlieh and Langmuir isotherm models. The adsorption capacity for GTFC by Rhodamine B dye was found to be 31.847 mg/g at an initial pH of 5±0.2 at 30 ± 2°C for the particle size of 125-250um.The complete removal of the dye for 20 mg/L and 30 mg/L of aqueous solution was possible with 6 and l()g of the activated carbon respectively. The percent removal of the dye was increased with decrease in the particle size of the adsorbent. The influence of pH on dye removal was insignificant and a portion of the dye from the dye laden carbon was recovered in basic medium, suggesting that the major mode of adsorption process follows is ion exchange mechanism.

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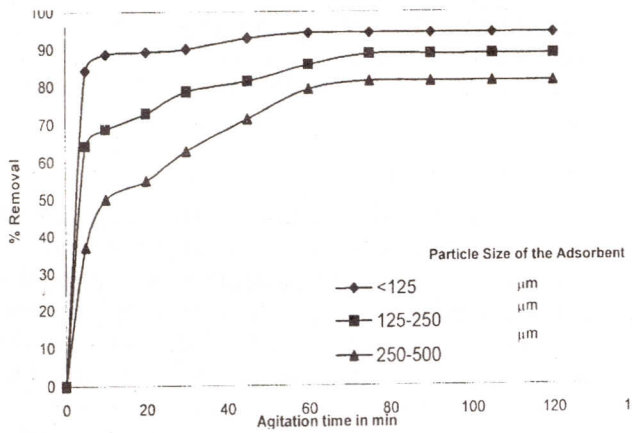

Fig. 7 Effect of particle size of the adsorbent on Rhodamine B adsorption.

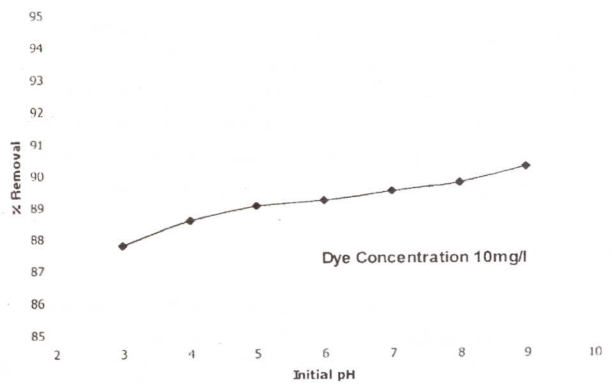

Fig. 8 Effect of pH on Rhodamine B adsorption.

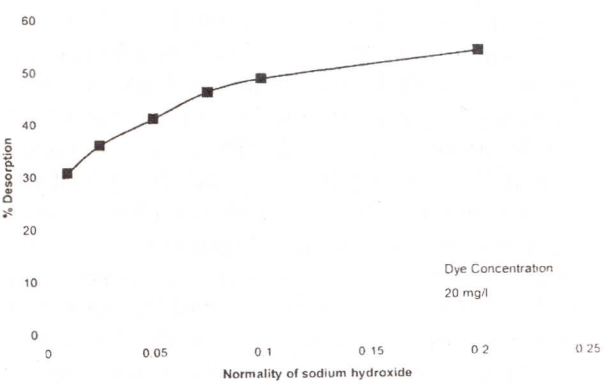

Fig. 9 Desorption studies of Rhodamine B adsorption.

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